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(54) A SILICON BRASS RESISTANT TO PARTING CORROSION

(71) We, THE ANACONDA COMPANY, a Corporation organized and existing under the laws of the State of Montana, United States of America, of 25 Broadway, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The addition of silicon to brasses increases the mechanical strength of the alloys making them more suitable for use as valve stems and other objects which are subjected to tensile and bending forces. Other desirable features of these alloys are machinability and their freedom from galling or seizing in operation.

However, the resistance of silicon brasses to the corrosive action of many waters and other corrosive fluids has not been satisfactory. For example, in some public water systems valve stems have failed within 1 to 2 years due to parting corrosion. This type of corrosion can be thought of as a leaching out of alloying agents leaving copper behind in a porous and weakened condition. This process of parting corrosion is usually referred to as "dezincification" when it occurs in the common copper-zinc brasses.

The problem of dezincification in valve stems has been recognized for years and it was particularly severe when high zinc alloys, such as manganese bronze with 40% zinc, were used. To combat this problem, manufacturers of valves turned to the silicon brasses which can contain from 5 to 22% zinc and over 0.5% silicon, but usually the range of 12 to 20% zinc and 2.5 to 4.5% silicon has been used. This approach is based on the premise that the lower zinc content would deter dezincification and to some extent it has been successful. However, the parting corrosion problem is again becoming serious because of lower water quality as a conse-

quence of the increasing demand for water due to increased population and industrial needs.

As a reaction to this corrosion problem, the trend once again is towards lower zinc levels. The disadvantages of smaller zinc contents are (1) increased cost of alloys and (2), what is more important, decreasing the zinc does not necessarily eliminate parting corrosion. It has been discovered that parting corrosion in silicon brass is not solely a function of zinc content but rather of both zinc and silicon.

Another approach has been the addition of arsenic, antimony, or phosphorus inhibitors which is known to reduce parting corrosion in single phase copper-zinc brasses, but the use of such inhibitors had been found to be ineffective for two-phased copper-zinc brasses. Since most silicon brasses depend upon multiphase structure to produce high mechanical strength, the benefits of these inhibitors would not have been predicted, nor would such additions have appeared promising. Furthermore, it has not been appreciated that silicon additions aid parting corrosion of even alpha phase, the primary structure, and therefore no prior attempts to negate the effect of silicon have been made.

Copper-zinc alloys containing small amounts of silicon in the range of 1% to 2.5% silicon, depending on zinc content, are resistant to parting corrosion. However, when the silicon content is increased for strength purposes above these levels to amounts in the range of greater than 2.5% to 7%, depending on zinc content, parting corrosion will occur. To overcome the corrosion disadvantage of higher silicon levels, arsenic, antimony or phosphorus will provide the alloy with substantial immunity to parting corrosion, whether the alloy is single or multiphased, if proper heat treatment is performed on cast or wrought material.

The invention provides a silicon-brass alloy resistant to parting corrosion consisting of

3—21% by weight zinc, an amount of silicon in the range of 2.5 to 6%, said amounts of zinc and silicon being sufficient to produce a structure consisting of alpha plus zeta phases in the brass, from 0.030% up to the percentage by weight of solid solubility of one or more elements of the group consisting of arsenic, antimony and phosphorus, remainder copper, said alloy having been rapidly cooled to room temperature from a temperature in the range of 500°C to 760°C and exhibiting an alpha plus zeta micro structure.

The principal of operation of the present invention is the selection of proportions of copper, zinc, silicon and inhibitors within ranges depicted by areas bordered by dashed lines on the Figures. The dashed-lined areas disclose the alloys which under commercial conditions of heat treatment are protectible by inhibition addition. These areas of the Figures show the alpha-zeta phase for alloys held at temperature for short periods of time prior to quenching while the solid-line phase boundaries show the phases, including the alpha-zeta phase as indicated, obtained when the alloys are held for long periods, such as days, at selected temperatures to permit an equilibrium condition to be reached.

The upper end of the range of inhibitor is the percentage just below that at which the inhibitor will start to precipitate and form compounds that may have deleterious effects. While percentages above 0.10% are not generally required, the addition of amounts of inhibitors above 0.10% does not adversely affect the alloy until the percentage of solid solubility is passed.

Figs. 1, 2 and 3 of the drawings show parting corrosion behavior for three different alloy conditions plotted on the copper-rich corner of the ternary alloy system of the present invention. Fig. 4 shows the phases formed when the alloy is cooled from a temperature below 500°C.

Figs. 1, 2 and 3 show the copper-rich corner of the ternary system of copper, zinc and silicon and whether an alloy having a particular composition undergoes parting corrosion with, or without, an inhibitor present in a specific water, and under electrochemical conditions that will be described below. The areas defined by the dashed lines denote compositions which were tested and found to suffer parting corrosion in the absence of an inhibitor. For example, in Fig. 1 it is seen that an alloy P, whose composition is 8% zinc, 3% silicon, and balance copper, and cast using normal commercial procedures, would suffer parting corrosion. However, in accordance with the invention, the addition of at least 0.03% inhibitor provides substantial immunity to parting corrosion.

The solid lines of Figs. 2, 3 and 4 are the equilibrium phase boundaries as deter-

mined by Horace Pops (Trans. Met. Soc., AIME, 230, 813—820, 1964). The significance of these diagrams is that they define the phases that would exist if the alloys were allowed to remain at these temperatures for long periods of time such as days or weeks depending on the temperature. No equilibrium phase boundaries are shown in Fig. 1 since cast alloys are generally produced under non-equilibrium conditions.

In commercial operations, the alloys of this invention are cast, then heated and further processed by extrusion and drawing. Such treatments do involve high temperatures, such as 500 to 750°C, but the length of time of treatment is generally only a few hours in duration and equilibrium is never attained. Thus, it is quite common to find, for example, alpha and zeta phases existing in alloys where only alpha would be predicted from the phase diagram. However, the phase diagram provides an excellent base on which to describe metallurgical phenomena.

In Figs. 2 and 3 it will be noted that the area bounded by the dashed lines involved three phases, alpha, beta, and zeta. However, beta in this region of composition is stable only at high temperatures and attempts to retain it by very rapid quenching fail; it quickly transforms to a mixture of alpha and zeta. On the other hand, alloys consisting of alpha or alpha and zeta at these higher temperatures can be quenched so that these same phases remain intact at room temperature. Thus commercial alloys quickly cooled or quenched from above 500°C commonly consist of alpha and zeta phases even though only alpha or alpha and beta would be predicted from the phase diagram.

Below about 500°C, depending on the composition, zeta phase is no longer stable and transforms either into mu or chi as shown in Fig. 4. In the temperature range of 400—500°C, the kinetics of the transformation of zeta are fast enough to produce significant amounts of mu and chi in minutes. These phases cannot be protected from parting corrosion, even with inhibitors present, and so they are highly undesirable from the corrosion resistance standpoint. Alpha, of course, can be protected by inhibitor as has been known for years. The unexpected discovery that zeta phase can also be inhibited is the basis for this invention. Thus, with proper inhibitor addition and temperature control, silicon brass alloys manufactured either in the cast or wrought form can be made resistant to parting corrosion so long as only alpha and zeta phases exist in the final state.

The parting corrosion test used to develop the data herein employed an electronic potentiostat, an instrument which allows corrosion reactions to occur under carefully defined electrochemical parameters. This test more closely parallels actual service conditions than

past procedures using hydrochloric acid or copper chloride solutions which are extremely aggressive and not therefore typical of conditions found in water distribution systems.

- 5 The tests were carried out under an argon cover for 24 hours at zero millivolts referenced to a saturated calomel electrode. Cylindrical specimens were 10 millimeters in diameter and about 20 millimeters long. Room temperature test water was used, but, if no parting was detected, the test was again run at 52°C and, if still no parting was found the specimen was categorized as showing no parting. These tests were found to correlate well with actual experience with a variety

of uninhibited alloys which had been in service for years in aggressive potable waters. Where an alloy specimen passed both the room temperature and 52°C test, it can be predicted that it would perform well in service in a corrosive water condition. The potentiostatic tests were carried out using a test water having similar composition and characteristics of Colorado River water which is an aggressive potable water used in large quantities in the Southwestern region of the United States. The composition of the test water and Colorado River water is set out in the following table.

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TABLE I

	Total Dissolved Solids	Test Water 680—730 ppm	Colorado River Water 650 ppm
35	Total Hardness (CaCO ₃)	122—170	125
	Alkalinity	110—122	109
	SO ₄	286—293	214
	Cl	92—104	80
	NO ₃	2	0.5
40	Ca	46—48	32
	Mg	1—13	11
	Na	170	172
	K	5	4
45	Conductance (micromhos/cm)	1000—1100	1021
	pH	7.8—8.1	8.35

- 50 In compiling the corrosion data set forth on Fig. 1, alloys having the ranges of zero to 24% zinc, 1% to 6% silicon, up to 0.06% of an inhibitor and with the remainder copper were cast into specimens which were then rapidly cooled to room temperature. Each specimen was thereafter tested to determine if

the test water would cause any detectable parting corrosion. The criterion for determining the occurrence of parting was metallographic examination. The following table includes the composition of a number of specimens tested and states whether parting corrosion was detected.

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TABLE II

Compositions of Cast Alloys and Results of Parting Corrosion Test

				Parting			
65	Cu	74.01	78.87	82.71	93.54	95.51	94.10
	Zn	24.64	17.22	13.41	3.63	—	—
	Si	1.35	3.91	3.87	2.83	4.49	5.72
	As	—	0.01	0.01	—	—	0.056
				No Parting			
70	Cu	79.23	78.69	82.74	86.54	89.07	
	Zn	17.45	17.45	13.34	8.68	6.28	
	Si	3.23	2.81	3.88	4.74	4.61	
	As	0.05	0.05	0.03	0.03	0.04	

- 75 The corrosion data depicted in the ternary phase diagrams of Figs. 2 and 3 was obtained in the same manner as described in obtaining data for the diagram of Fig. 1, except that the cast specimens were swaged, encap-

sulated, annealed at 600°C for 10 days and 760°C for 5 days and then quenched. Compositions of some of the specimens tested and the results of the tests are set forth below in Table III.

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TABLE III

Parting						
5	Cu	77.9	78.0	79.30	82.79	89.03
	Zn	20.3	19.52	17.34	13.37	6.38
	Si	1.83	2.50	3.35	3.83	4.59
	As	—	—	0.005	0.005	—
No Parting						
10	Cu	76.96	78.79	82.58	89.07	
	Zn	19.66	17.24	13.47	6.28	
	Si	3.32	3.93	3.90	4.61	
	As	0.06	0.03	0.05	0.04	
15	Cu	82.06	Cu	82.11		
	Zn	19.94	Zn	13.82		
	Si	3.96	Si	3.98		
	P	0.04	Sb	0.088		

The effect of annealing specimens at 760°C was to require the use of more inhibitor at the higher zinc and silicon contents to provide immunity to parting corrosion, as illustrated by the upper dashed area on the Figures. Annealing at 600°C reduced the requirement of using a larger amount of inhibitor until the zinc content reached over 19%. Other samples were annealed at various temperatures between 550°C and 760°C and it was found that the immunity to parting obtained was substantially as illustrated on Figs. 2 and 3. If, however, alloys are annealed or slowly cooled below about 500°C, mu and chi phases will occur which are highly susceptible to parting. These phases, as mentioned earlier, cannot be protected by an inhibitor, thus it has been found essential to quickly cool castings or wrought material from over 500°C to prevent these phases from forming.

corrosion consisting of 3—21% by weight zinc, an amount of silicon in the range of 2.5 to 6%, said amounts of zinc and silicon being sufficient to produce a structure consisting of alpha plus zeta phases in the brass, from 0.030% up to the percentage by weight of solid solubility of one or more elements of the group consisting of arsenic, antimony and phosphorus, remainder copper, said alloy having been rapidly cooled to room temperature from a temperature in the range of 500°C to 760°C and exhibiting an alpha plus zeta micro structure.

2. A silicon brass alloy as claimed in claim 1 and substantially as herein described, with reference to the Examples.

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WHAT WE CLAIM IS:—

1. A silicon brass alloy resistant to parting

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